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METHODS FOR DETERMINING THE UNIFORMITY OF QUALITY OF WHITE SUGARS

Including Analytical Methods for Massecuites and Juices

Compiled by J. A. Ambler, Chemist

Carbohydrate Research Division

May 1940

METHODS FOR DETERMINING THE UNIFORMITY OF QUALITY OF WHITE SUGARS

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In response to numerous requests for the methods used in the Carbohydrate Research Division, Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture, for the determination of the quality of sugars and of the quantities of various non-sugars present in sugars, massecuites and sugar plant juices, the descriptions of the methods and technic for the various determinations were assembled and issued in 1934 under the title "Methods of Analyzing White Sugars, Massecuites and Juices." Since then new determinations have been added and some of the others have been revised, making necessary a revised compilation. For the development of the methods given the publications cited should be consulted, since the following pages describe only the procedures in use.

These methods are not to be considered as in any way official, since there are in many cases alternative technics which would, no doubt, be equally satisfactory; they are, rather, the methods which have been adopted in this Division for the determinations necessary in studying impurities in white sugars and the effects of these impurities on the quality of the sugar. In pursuing such studies over a period of years, it is necessary, in order to obtain comparable

results, to adopt for each determination a definite technic which yields comparable and uniform results, insofar as this is possible. Of the many methods described in the chemical literature for many of these determinations, the procedures described have proved satisfactory in this respect and have been successfully used for several years.

METHODS OF TESTING WHITE SUGARS

FOAMING TEST

Paine, Badollet and Keane, Ind. Eng. Chem., 16, 1252 (1924).

To 50 gms. of sugar in a 200 ml. beaker, tall type, add 25 ml. of water. Suspend a thermometer over the beaker so that the bulb is immersed in the sugar-water magma. Heat gradually to 117.8° C. (244° F.) without stirring and at such a uniform rate that the times required to reach the first boiling point and 117.8° C. are 3.5 to 4 minutes and 8 to 9 minutes, respectively. When boiling starts, mark on the outside of the beaker the level of maximum foaming. Similarly mark the level of maximum foaming when the temperature has reached 117.8° C. Discard the sugar solution, rinse the beaker and determine with the aid of a measuring cylinder the volumes corresponding to the two marks on the beaker. Express the results as the number of milliliters at maximum foaming on first boiling and the number of milliliters at maximun foaming at 117.8° C.

It facilitates the manipulations to use 200 ml. beakers, tall type, which are graduated, in 5 ml. intervals, from 60 ml. to 200 ml.

SCREENING TEST

The grain size of sugars is determined by sieving 500 gms. of sugar through a nest of screens which is mechanically agitated for six minutes. The sieves used in order of size (meshes to the inch) are as follows: 20, 28, 35, 48, 60, 65, 80, and 100, corresponding to U. S. Series equivalent Nos. 20, 30, 40, 50, 60, 70, 80, and 100. The amount of sugar retained on each sieve, as well as the amount passing through the 100-mesh sieve, is weighed and calculated as percentage.

MEASUREMENT OF pH

Unpublished

The pH of white sugars is determined colorimetrically in a solution of 15 gms. of sugar per 100 ml. in neutral water.

Several methods of preparing neutral water have been recommended from time to time. For use with sugars in the determination of pH, the following technic has been found to yield, without undue trouble, results which are constant, easily reproduced and sufficiently accurate for this work. Neutral water cannot be kept and therefore must be made fresh just before use.

The apparatus consists of a large pyrex round-bottom blask, fitted with a Kjeldahl connecting bulb which is connected by a rubber stopper to the top of a pyrex condenser. The latter is connected in an air-tight manner with a large pyrex receiving flask carrying an absorption or drying tube charged with soda-lime to provide for equalization of the pressure in the system with that of the atmosphere and at the same time to protect the whole system from the carbon dioxide of the air.

Fill the flask with distilled water and add an excess of solid barium hydroxide. Distill one-sixth to one-fifth of the original volume and discard the distillate. Distill another 200 or 300 ml. and rinse the receiver thoroughly with the distillate and discard it. Distill three-fifths of the liquid remaining in the distilling flask, remove the distillate and rapidly boil off one-third of its volume. Fill an Erlenmeyer flask full with the hot water, invert a clean beaker over the top of the flask, and cool rapidly under running cold water. When cooled and tested as described below, this water shows a pH of 6.9 to 7.0.

Place 15 gms. of sugar in a clean, dry, 100 ml. glass-stoppered pyrex volumetric flask. Fill to slightly below the stopper with the cold neutral water, using a pipet and keeping the tip just above the surface of the sugar and liquid. Fill an empty flask in the same manner to serve as a control. As soon as a flask is filled, close it tightly to prevent circulation of air over the liquid in the flask. Dissolve the sugar by inverting and shaking the flask.

Pipet 10 ml. into a clean comparison tube containing 0.5 ml. of the proper indicator solution, keeping the tip of the pipet just below the surface of the indicator solution. Close the tube with the thumb and mix by slowly inverting the tube twice. Compare the color of the solution with that of colorimetric standard solutions in the usual way. For sugars, the proper indicator generally is bromthymol blue; for barley candies, bromcresol green. These indicators and standard comparison solutions and comparators are obtainable from chemical supply houses. An assortment of indicators and standards for pH ranges from 4.0 to 7.6 should be obtained.

COLOR

Ambler and Byall, Ind. Eng. Chem. (Anal. Ed.), 3, 135 (1931).
Balch, Ind. Eng. Chem., 22, 255 (1930).

The color of a solution of sugar containing 60 gms. of sugar per 100 ml. is compared in a colorimeter with a solution of caramel of known color strength. Balch has defined the color standards for maple sirup in terms of caramel in such a way that these standards are capable of ready reproduction. Since in the great majority of cases the color of sugars is due to adhering films of molasses or sirup which have a color practically the same as that of caramel, it has been found possible to compare all white sugars with diluted solutions of Balch's maple sirup standards, except those sugars which have a gray color due to colloidal carbon. For

white sugars, Balch's #5 standard has been found appropriate, and for barley candies the #9 standard has been chosen.

Balch's #5 maple sirup color standard is defined as a solution of 4.00 gms. of standard caramel in 96.00 gms. of glycerine and has a transmission to light of 560 mμ wave-length, in a 1 cm. cell, of 82.5%; the #9 standard is a solution of 12.57 gms. of standard caramel in 87.43 gms. of glycerine and has a transmission to light of 560 mμ wave-length, in a 1 cm. cell, of 53.0%. Measured in a Pfund color grader, #5 standard reads 40 mm. and #9 reads 87 mm. Since each batch of caramel varies in color strength, the caramel itself must be standardized according to the table and charts given in Balch's article.

For determining the color of white sugar, make the standard solution by diluting 10 gms. of the #5 standard caramel solution with water to a volume of 100 ml. and place the solution in one side of a Campbell-Hurley (or similar) colorimeter which is set up in a dark place and illuminated by a standard daylight lamp. Dissolve 120 gms. of sugar in cold distilled water and make up to 200 ml. Add 15 to 20 gms. of standard Filter Cel, mix thoroughly and filter through paper on a small Büchner funnel. Place the clear filtrate in the other side of the colorimeter and determine the color by finding the volume of the standard solution which matches in color 100 ml. of the filtered sugar solution. This method of reading gives a direct measure (percent of the color in the standard solution) of the amount of coloring matter present in the sugar solution. If the sugar solution is darker than the standard, match the color of 50 ml. (or, if necessary, of 25 ml.) of the sugar solution against the standard and multiply the reading by 2 (or by 4).

For the color of barley candies, dilute 10 gms. of Balch's #9 standard caramel solution to 100 ml. with water and determine the color of a filtered solution of 30 gms. of candy made up to 200 ml. with water, in exactly the same way as described for the determination on white sugar.

Since no relationship between color of the sugar and color of the barley candy has been found, it is not necessary to use the same standard solutions, or the same concentrations of the unknown. The colors of the sugar and the candy are expressed in different units for convenience but, if necessary, by suitable calculations allowing for the different concentrations of caramel in the two standards and of solids in the solutions of sugar and candy, the values may be converted into expressions based on a common unit.

Alternate Method:

Color determinations in recent years have been made by means of the photometer developed for sugar work by B. A. Brice and J. C. Keane. This method is described under "Reflectance, Color and Turbidity."

TURBIDITY

Balch, Ind. Eng. Chem. (Anal. Ed.), 3, 124 (1931).

The principles involved and the apparatus used are the same as for the spectrophotometric analysis of color. Turbidity in the solution of a white sugar is determined as the -log t value of an unfiltered portion of a solution of the sugar, measured against a clear, filtered portion of the same solution in order to compensate for color. According to Balch, Lambert and Beer's law, used in spectrophotometric analysis, "does not hold exactly for turbid solutions. Until it is possible to develop more adequate relationships, it is proposed to assume the validity of Lambert and Beer's law and to express turbidities as -log t values in accordance with the equation,

$$-\log t = \frac{1}{cb} (-\log T)$$

where t = transmittancy reduced to unit conditions as regards concentration and thickness of solution; c = concentration of the solution expressed as grams of dry substance per 1 cc; b = thickness of solution expressed in cm; and T = the transmitted fraction of the incident light." The measurement is made at 560 mμ.

Dissolve 60 gms. of sugar in cold distilled water and make up to 100 ml. and mix thoroughly. Fill one cell of the spectrophotometer with a portion of this solution. To the rest of the solution add about 3 gms. of Filter-Cel, mix thoroughly and filter by suction through paper on a small Büchner funnel which is attached to a fractional distillation receiver. Collect 15 to 20 ml. of filtrate, and then change the container without disturbing the vacuum. The last portion should appear brilliantly clear by transmitted light of ordinary intensity. Fill the second cell of the spectrophotometer with this clarified solution and determine the fraction of transmitted light of 560 mμ wave-length which passes through the unfiltered solution as compared with the clarified solution. Calculate the -log t value by the equation given above.

For the determination of the "Citric Acid Turbidity," make the same determination on a solution of 60 gms. of sugar and 1.68 gms. of citric acid per 100 ml. after the solution has stood at room temperature for 24 hours.

Different turbidity values will be obtained if other concentrations of sugar are used.

Alternate Method:

Turbidity determinations in recent years have been made by means of the photometer developed for sugar work by B. A. Brice and J. C. Keane. This method is described under "Reflectance, Color and Turbidity."

REFLECTANCE, COLOR AND TURBIDITY

Keane and Brice, Ind. Eng. Chem. (Anal. Ed.), 9, #6, 258 (1937).
National Bureau of Standards Letter Circular LC-395, Jan. 20, 1936.

Working in cooperation, B. A. Brice, formerly of the Food and Drug Administration, and J. C. Keane, formerly of the Carbohydrate Research Division, Bureau of Chemistry and Soils, developed a photoelectric apparatus known as the Brice-Keane Sugar Photometer. With this instrument it is possible to measure not only the reflectance of sugar in granular form, but also the transmittancy of sugar solutions, so that it is possible to obtain (1) an index of appearance for the crystalline sugar in terms of reflectance; (2) an index of apparent color of the unfiltered sugar solution in terms of transmittancy for green and red light; and (3) an index of turbidity of the solution in terms of transmittancy for red light.

Reflectance:

It is customary in reporting reflectance measurements to express the reflectance of a sample relative to that of magnesium oxide. But, as a surface of MgO is not permanent and should be freshly prepared at frequent intervals, it is not a convenient standard for use in practice. A rugged and permanent reference standard which can be readily cleaned is a solid white opal glass with a finely ground surface. The reflectance of such a reference standard is first determined in the apparatus relative to a freshly prepared MgO surface. This reference standard is then used for all subsequent reflectance measurements on sugars, and by proper setting of the scale of the instrument all reflectances of sugars are read off directly in terms of MgO.

The following procedure for preparing a surface of the sugar sample for a reflectance determination has been found to give reproducible results.

An excess of sugar is poured into a metal dish 2-1/2 inches in diameter and about 3/4 inch deep, and the entire surface of the sugar is made plane and flush with the edge of the dish by means of a 3-1/2 inch Petri dish with a finely ground plane bottom. Great care in preparing this surface is of the utmost importance since even slight over-filling or under-filling of the dish affects the measured reflectance appreciably due to the nearness of the photronic cell and the well known fact that light intensity varies inversely as the square of the distance.

The procedure in making a reflectance determination with the photoelectric instrument is as follows: With the standard reference plate in position to intercept the light beam, the galvanometer set on zero, and the slide-wire scale set at the value found for the reflectance of the reference plate relative to MgO, the lamp is turned on. The galvanometer indicator is then made to read zero by adjusting a shutter which controls the intensity of light falling on the compensating photronic cell. The sugar sample is then slid into the light beam to replace the reference plate, and the galvanometer made to read zero by adjusting the slide-wire. The scale reading of the slide-wire then indicates the reflectance of the sugar sample relative to MgO. Three determinations are made on each filling of the dish; three more are made on a second filling with the same sample. The figures reported are the average of the 6 determinations made on each sample of sugar. They are expressed to four significant figures. For practical purposes one reading on each of two fillings would probably be sufficient, in which case only three significant figures should be expressed in the result.

Color and Turbidity:

The photoelectric method for determining the apparent color and turbidity in sugar solutions without recourse to filtration offers a simple,

rapid evaluation of quality for the purpose of industrial control. The determination of apparent color in the unfiltered solutions is based on the fact that with increasing amounts of yellowish coloring matter the ratio of green to red transmittancy, T_g/T_r, should decrease. If the suspended matter in the solution were to scatter light non-selectively, this ratio would be independent of turbidity. In sugar solutions for which a varying proportion of the scattered light is selective, however, this ratio is not entirely independent of the suspended matter, and the ratio T_g/T_r may be taken to indicate only the apparent color. The form adopted for the apparent color index is $I_c = 100\ (1 - T_g/T_r)$, since in this form $I_c = 0$ for a hypothetical sugar free from coloring matter and turbidity and increases with increasing amounts of coloring matter. This color value could be expressed by the difference between the specific absorptive indexes for green and red light, but since the instrument scale indicates transmittancy, and since only a practical quality index for solution of constant depth and concentration is desired, it is believed there would be no advantage in using the more usual logarithmic form of expression.

The turbidity index is $I_t = 100\ (1 - T_r)$, which is the percent absorbency of the unfiltered sugar solution for red light. This index is practically independent of the coloring matter in solutions of white sugar, because there is virtually no light absorption in the red part of the spectrum by the small amount of coloring matter present. In this form $I_t = 0$ for a hypothetical sugar solution free from suspended matter and having a relatively small quantity of coloring matter and would increase with increasing turbidity. Expressed in the form of specific absorptive index, $(-\log T_r)/bc$, where (b) is the depth of solution in cm. and (c) is its concentration in grams per ml. of solution, the results were found to be in agreement with the values obtained by Balch's method.

The procedure for the transmittancy measurements is as follows: 150 gms. sugar are dissolved in distilled water at room termperature and made up to 250 ml. of solution. The minute bubbles of occluded air present in a freshly prepared solution may be removed by applying vacuum or allowing the solution to stand for several hours. The solution is transferred to a 150-mm. absorption cell having plane and parallel ends and placed in the instrument. Another absorption cell, similar to, but only half as long as, the solution cell, is filled with distilled water from the same source as that used in making the solution and used as the reference cell for the transmittancy measurements.

A 150-mm. solution cell is used because of the small amount of coloring matter present in white sugar. A solvent cell approximately half this length is used because the concentrated sugar solutions contain only 51.2% water, and water of this depth appreciably absorbs the red light transmitted by the red filter used in measuring transmittancy of the solution for red light. Therefore, a reference cell 75 mm. long and containing distilled water very nearly compensates for selective absorption of red light by the water in the solution as well as for reflection losses at the glass surfaces of the cell.

In determining the color of the barley candies, 37.5 gms. of candy are dissolved in distilled water and made up to 250 ml. In this case, because of the greater amount of coloring matter and the low concentration of solids, a 75-mm. cell is used for the solution cell as well as for the reference cell.

In making transmittancy measurements the scale is set to read 100 with the standard white plate and water cell in the light beam. After the circuit is balanced, the water cell is replaced by the solution cell, and

when the circuit is rebalanced, the scale indicates the transmittancy of the solution. The transmittancy of each unfiltered sugar solution is measured first with a blue-green filter and then a red filter. The apparatus and method are described in detail in the publication by Keane and Brice. Sugar photometers of this type are now on the market.

SULFUR

Modified from Method of
Ambler, Snider and Byall, Ind. Eng. Chem.
(Anal. Ed.),3, 339 (1931).

I. Sulfates

Prepare with distilled water a stock solution of solvent containing approximately 0.01% of sulfuric acid and 50 ml. of concentrated hydrochloric acid per liter. Dissolve 100 gms. of sugar in 200 ml. of this solution, add 10 ml. of 10% barium chloride solution. Mix thoroughly and allow to stand overnight. Collect the precipitated barium sulfate on a tared Gooch crucible, wash with hot distilled water, ignite, cool and weigh as usual. Run a blank determination of sulfates on 200 ml. of the stock solution. Subtract the weight of barium sulfate obtained from the blank on the stock solution from the weight of barium sulfate found in the sugar solutions and calculate the difference as SO_3, parts per million of sugar.

II. Sulfites

(a) Inorganic Sulfites:

Dissolve 100 gms. of sugar in 135 to 150 ml. of distilled water in an Erlenmeyer flask. Add a few milliliters of starch solution. Remove the oxygen dissolved in the solution by passing a rapid stream of nitrogen through the solution for at least 10 minutes. Stop the stream of nitrogen and immediately add 5 ml. of 1:3 sulfuric acid and titrate

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rapidly with 0.01 N iodine solution to an end point which is permanent for at least 2 minutes after four or five rotations of the flask. Determine the iodine consumed in a blank determination on water and reagents and deduct from the titer of the sugar solution. Calculate as SO_2, parts per million of sugar.

(b) Total Sulfites:

Dissolve 100 gms. of sugar in 125 to 150 ml. of distilled water in an Erlenmeyer flask. Add a few milliliters of starch solution and 25 ml. of 1 N potassium hydroxide solution. Remove oxygen as under "(a)", add 10 ml. of 1:3 sulfuric acid, mix and immediately titrate rapidly with 0.01 N iodine solution as before. Make a blank determination on water and reagents and deduct the value from the titer of the sugar solution. Calculate as total SO_2, parts per million of sugar.

(c) Organic Sulfites:

Subtract the value found under "(a)" from that found under "(b)".

PHOSPHORUS AND SILICA

Byall and Ambler, Ind. Eng. Chem. (Anal. Ed.), 4, 325 (1932).

Reagents:

Molybdate Solution: - Dissolve 25 gms. of ammonium molybdate in 300 ml. of water and to this add 200 ml. of water containing 75 ml. of concentrated sulfuric acid.

Hydroquinone Solution: - Dissolve half a gram of hydroquinone in 100 ml. of water to which a drop of sulfuric acid has been added to retard oxidation.

Sulfite Solution: - Dissolve 20 gms. of sodium sulfite in 100 ml. of water. Use only a freshly prepared solution.

Mixed Anhydrous Carbonates: - Mix intimately equal parts of pure anhydrous sodium and potassium carbonates and keep stoppered as a stock reagent.

Concentrated Nitric Acid: - Sp. gr. 1.42.

Acetic Acid Solution: - 20% by volume.

Standard Phosphate Solution: - Dissolve 0.4394 gm. of potassium dihydrogen phosphate in water and dilute to 1 liter. Dilute 25 ml. of this solution to 200 ml. This gives a solution which contains 0.0287 mg. of P_2O_5 per ml.

Standard Silicate Solution: - Determine gravimetrically the percentage of SiO_2 in a solution of water glass. Weigh a portion of the water glass solution sufficient to contain 0.725 gm. of SiO_2 and dilute with distilled water to 1 liter. Dilute 5 ml. of this solution to 100 ml. with distilled water. Both of these silica solutions must be made fresh on the day they are to be used, since on standing the silicate hydrolyses to silicic acid, which becomes colloidal and nonreactive. The solution of water glass from which these solutions are made should be limpid, and should be taken from a previously unopened bottle. The dilute solution contains 0.0363 mg. of SiO_2 per ml. and is equivalent to the standard phosphate solution.

Preparation of Colorimetric Standards: - The standards for the colorimetric comparison are developed simultaneously with the unknowns. Since the silica standard is equivalent to the phosphate standard, only the latter need be used in analyses, which obviates the uncertainty liable to be encountered concerning possible deterioration of the silica standard and also saves time and expense. Place measured volumes ranging from 0.1 to 4.0 ml. of the standard phosphate solution in 100 ml. Nessler

tubes. To each add, in the order given, 5 ml. of the molybdate solution, 1 ml. of the sulfite solution, 1 ml. of the hydroquinone solution, and enough distilled water to make a final volume of 100 ml.; mix and allow to stand for 30 minutes.

Procedure:

P_2O_5 Plus SiO_2: - Mix 5 gms. of sugar with 0.2 gm. of the anhydrous mixed carbonates in a platinum dish which just previously has been thoroughly cleaned by fusion of a considerable quantity of the carbonates. After burning the mixture to a white ash by careful charring followed by incineration at 550° C. in an electric muffle, fuse the residue over a free flame to a clear liquid melt. After the melt has cooled, dissolve it in about 15 ml. of cold distilled water, acidify with 1 ml. of the dilute acetic acid (which just neutralizes the carbonates), and transfer without filtering to a 100 ml. Nessler tube. Develop the color by the addition of the molybdate, sulfite, and hydroquinone solutions as described above, and after 30 minutes compare colorimetrically with standards which were developed simultaneously from the standard phosphate solution. Iron in the sugars caused a yellowish tinge, which is conveniently equalized by viewing both the standards and the unknown through a yellow Wratten light filter (K-3 No. 9). Record the result as the number of milliliters of the standard solution which matches the unknown, and correct for the amount of P_2O_5 plus SiO_2 found in the reagents in a blank determination.

Total P_2O_5: - Ash 5 gms. of the sugar with 0.2 gm. of the mixed carbonates as in the preceding determination, but do not fuse. After it has cooled dissolve in a little water and acidify with concentrated nitric acid. Render the silica insoluble by evaporating the solution to dryness on the steam bath, moistening the residue thoroughly with concentrated

nitric acid, again evaporating to dryness, and taking up in a little water. Filter the solution immediately to remove the separated silica, and collect the filtrate and washings together in a 100 ml. Nessler tube. Develop the color and measure as before, record similarly, and correct for the total P_2O_5 found in the reagents in a determination made on them alone.

Inorganic P_2O_5:- Dissolve 10 gms. of the sugar in a little water in a Nessler tube. Add to this the molybdate, sulfite, and hydroquinone solutions. Develop and measure the colors, correct for inorganic P_2O_5 in the reagents, and record the results as described above.

Calculation of Results:

SiO_2: - Subtract the value obtained in the determination of total P_2O_5 from that obtained in the determination of SiO_2 plus P_2O_5 and multiply the result by 0.0363. This gives the weight of SiO_2 in milligrams, from which the parts per million are obtained by multiplying by 200.

Organic P_2O_5: - Subtract one-half the value obtained for the inorganic P_2O_5 from that obtained for the total P_2O_5 and multiply the result by 0.0287. This product multiplied by 200 gives the parts per million.

Inorganic P_2O_5: - Multiply the corrected value found for inorganic P_2O_5 by 0.0287 and again by 100 to obtain the parts per million.

CHLORIDES

Ambler and Byall, Ind. Eng. Chem. (Anal Ed.), 4, 379 (1932).

Dissolve 100 gms. of sugar in about 150 ml. of distilled water and add about 0.5 ml. of saturated potassium chromate solution. Titrate with 0.01 or 0.02 N silver nitrate solution to the first permanent tinge of orange. Calculate to Cl, parts per million of sugar.

ASH

"Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists" (1935 Ed.), Section XXXIV, 8, p. 465.

Char, in a tared platinum dish, 100 gms. of sugar and incinerate to as white an ash as possible in an electric muffle furnace heated to 550° C., making sure that all carbon has been destroyed. Cool in a desiccator and weigh.

Save the ash for the determination of calcium oxide.

CALCIUM OXIDE

"Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists" (1935 Ed.), Section XXVI, 18, p. 323.

Take up the ash of 100 gms. of the sugar in 1 ml. of concentrated hydrochloric acid and 10 to 15 ml. of hot distilled water. Dilute to about 150 ml. in a 400 ml. beaker. Add 8 to 10 drops of bromcresol green indicator and sufficient 20% sodium acetate solution to change the pH to 4.8 to 5.0 (blue color of indicator). Cover with a watch glass and heat to boiling. Precipitate the calcium slowly by adding a 3% solution of oxalic acid, a drop at a time, every 3 to 5 seconds, until the pH is changed back to 4.4 to 4.6 (the optimum for calcium oxalate precipitation), as indicated by the appearance of a distinct green shade. A change of color will indicate an excess of oxalic acid - more would develop yellow tints, showing an undesirable displacement of the pH. Boil 1 to 2 minutes and allow to settle until clear. Filter and wash thoroughly with hot water. Determine volumetrically the calcium oxide in the precipitate by suspending precipitate and paper in 150 to 200 ml. of distilled water, adding 5 ml. of concentrated sulfuric acid, heating to 70° to 80° and titrating oxalic acid with 0.01 N permanganate. Calculate as CaO, parts per million of sugar.

SODIUM AND POTASSIUM OXIDES

Preparation of Material:

Ambler and Holmes, unpublished.

Ash 100 gms. of sugar (or an amount sufficient to yield 0.02 gm. of ash; 20 gms. of press juice; 3 gms. of massecuite) in an electric muffle at 550° C., lixiviating when working with juices and massecuites. Take up the white ash in 5 ml. of distilled water and 5 ml. of concentrated HCl. Evaporate to dryness on the steam bath, take up residue in 5 to 10 ml. of distilled water and filter immediately from the separated silica. Wash filter and dish thoroughly, making a total volume of 30 to 40 ml. Add 1 ml. of 10% barium chloride solution to remove sulfates (more may be added if necessary). Mix thoroughly and add, without filtering off the barium sulfate, 1/2 ml. of concentrated ammonia and 1-1/2 ml. of 10% ammonium carbonate solution. (If more than 1 ml. of barium chloride was used it may be necessary to use more ammonium carbonate. Note that the same amounts of these reagents must be used in preparing corresponding blank determinations.) Mix, filter, wash thoroughly and evaporate filtrate and washings to dryness on a steam bath. Heat the dry residue at 550° C. until all ammonium salts have been volatilized. Cool and add 1/2 ml. of dilute HCl and transfer to a 50 ml. volumetric flask and make up to volume. Measure 20 ml. into each of two 50 ml. pyrex beakers. Each aliquot represents 40 gms. of sugar. Evaporate each aliquot to dryness. Blank determinations on the same volumes of reagents must be carried through the same operations, to determine the Na and K in the reagents. One of these aliquots is used for the sodium oxide determination and the other for the potassium oxide determination.

I. Sodium Oxide

From the method of Barber and Kolthoff, J. Am. Chem. Soc., 50, 1625 (1928).

Reagents:

(1) Make two solutions, A and B, as follows:

A. Dissolve 10 gms. of uranyl acetate and 6 gms. of 30% acetic acid in 65 gms. (or ml.) of distilled water.

B. Dissolve 30 gms. of crystallized zinc acetate and 3 gms. of 30% acetic acid in 65 gms. (or ml.) of distilled water.

(2) After the salts in A and B have been dissolved by warming, mix the solutions thoroughly and allow to stand 24 hours. Just before using the reagent, shake and filter the amount necessary, leaving some of the precipitate in the unused portion. This gives a solution of the reagent which is saturated at room temperature with the triple sodium-zinc-uranyl salt, formed from sodium present as an impurity in the salts and acid used in making the reagent.

Saturate some 95% ethyl alcohol with the triple sodium-zinc-uranyl acetate obtained by collecting and drying the precipitate formed by adding 10 ml. of the reagent to 1 ml. of a 0.005% solution of NaCl.

Procedure:

Take up the dried aliquot for the sodium determination in 1 ml. of distilled water and add 10 ml. of the reagent. (Note: The aliquot must not contain more than 8 mg. of Na nor more than 50 mg. of K. If more than 1 ml. of water is necessary to dissolve the aliquot, use 10 ml. of reagent per milliliter of water.) Mix thoroughly, cover with a

watch glass and allow the mixture to stand at least 30 minutes. Filter through a tared porous porcelain or sintered glass crucible, using very gentle suction from a water pump. As soon as the mother liquor has been sucked through, wash the precipitate five to ten times, each time with 2 ml. of the reagent, allowing the reagent to be completely removed each time, but do not allow the precipitate or crucible to become dry. Next wash five times with 2 ml. of the 95% alcohol which has been saturated with the triple salt, and finally wash generously with ether.

Dry the precipitate and crucible by sucking air through them. Wipe the outside of the crucible clean with a moist cloth, dry in air for 10 minutes or longer and weigh. The precipitate has the composition $(UO_2)_3.Zn.Na.(CH_3COO)_9.6H_2O$. The weight of the precipitate minus the weight found in the blank multiplied by 0.02015 gives the weight of sodium oxide in the aliquot originally taken. Calculate to Na_2O, parts per million of sugar.

II. Potassium Oxide

From the Method of Austerweil and Lemay,
Bull. Soc. Chem., 49, 1541 (1931).

Reagents:

(1) Make two stock solutions:

A. Dissolve 200 gms. of cobalt nitrate, $Co(NO_3)_2.6H_2O$, in 600 ml. of distilled water and add 200 gms. of glacial acetic acid.

B. Dissolve 400 gms. of sodium nitrite, $NaNO_2$, as free from potassium as obtainable, in 600 ml. of water.

(2) The day before the reagent is to be used, mix in an ice bath equal weights of the two solutions and aerate with a stream of air to remove the NO_2 fumes. Let stand overnight and in the morning

filter from the precipitate through paper.

Procedure:

Take up the dried aliquot for the potassium determination in 5 ml. of water and add a drop of 1:10 acetic acid. Heat just to a boil, remove from flame and immediately add slowly and with constant stirring 5 ml. of the reagent and 5 ml. of 95% alcohol. Allow the mixture to stand overnight and filter on a thick asbestos mat in a Gooch crucible. Wash with 10% acetic acid and finally with 95% alcohol. Dry at 100 to 105°, cool and weigh.

Theoretically, the precipitate is $K_2NaCo(NO_2)_6.H_2O$ and the factor for K_2O is 0.2074. However, since generally the weight of K_2O is high when this value is used, it is best to derive the proper factor from known weights of potassium nitrate or chloride, using carefully controlled and uniform technic. Calculate to K_2O, parts per million of sugar, after correcting for the K_2O found in the blank determination on water and reagents.

NITROGEN

Ambler and Byall, Ind. Eng. Chem. (Anal. Ed.), 4, 34 (1932).

I. Total Nitrogen

An excellent method for the determination of nitrogen in low-purity products by micro-Kjeldahl technic has been described by Stanek and Vondrak, but it is not convenient nor economical to submit to Kjeldahl digestion sufficient white sugar to yield enough ammonia for even a microtitration. Hence, resort was had to a Kjeldahl digestion on smaller amounts of sugar, followed by estimation of the ammonia in the distillate by means of Nessler's reagent. But here it was found necessary to modify the Kjeldahl technic because it was impossible to procure potassium sulfate sufficiently free from nitrogen.

Reagents:

Ammonia-free Water: - (1) Prepare what will hereafter be called "ammonia-free" water by boiling distilled water with very finely powdered magnesium oxide until the distillate gives no test with Nessler's reagent, and collecting the water which subsequently distills in ammonia-free containers. (Magnesium oxide is used here in preference to the more usual sodium hydroxide or carbonate because its suspensions boil more evenly if the oxide is very finely divided. For this purpose the finest powdered oxide obtainable is necessary, that which will pass in suspension through a 150-mesh screen.) Carry out the whole distillation in an atmosphere free from ammonia and its volatile compounds. Use the ammonia-free water so obtained for the preparation of the standard ammonium chloride comparison solutions and for aliquoting the distillate when necessary before Nesslerization.

(2) Prepare what will hereafter be referred to as "magnesia water" by concentrating to two-thirds or one-half its original volume a suspension of the finely powdered magnesium oxide in distilled water. Allow to cool and settle in an ammonia-free atmosphere. The clear or slightly turbid supernatant magnesia water is suitable for use as ammonia-free water in making solutions and in diluting solutions before distillation. It cannot be used for diluting a solution to which Nessler's reagent is to be added.

Copper Oxide: - Ignite powdered copper oxide to a bright red heat to burn off all nitrogenous matter. Cool and stopper closely to exclude ammonia and the condensation of ammonium salts from the air.

Sulfuric Acid: - Pure concentrated sulfuric acid of specific gravity 1.84.

Potassium Hydroxide Solution: - Using magnesia water, prepare a solution containing 200 gms. of potassium hydroxide (stick form) per liter.

Sodium Hydroxide Solution: - Prepare with magnesia water a saturaged solution of sodium hydroxide.

Nessler's Reagent.

Standard Ammonium Chloride Solution: - Dissolve exactly 1.9093 gms. of pure ammonium chloride in 1 liter of ammonia-free water. Dilute 20 ml. of this solution to 1 liter with ammonia-free water. The resulting solution contains 0.01 mg. of nitrogen as ammonia in each milliliter.

Apparatus:

The apparatus used is a regular Kjeldahl digestion and distillation outfit and ordinary 100 ml. Nessler tubes. Before each determination free the stills from nitrogen compounds by distilling a suspension of the finely powdered magnesium oxide in distilled or magnesia water until no color develops when 2 ml. of Nessler's reagent are added to 100 ml. of the distillate. This may take some time when the apparatus is first set up. Rubber stoppers or connections should be boiled out thoroughly with dilute sodium hydroxide solution before they are used. If the apparatus must be in a room where other chemical work is being carried on, it is necessary to perform all distillations in a system protected from ammonia by a trap containing acid and, when not in use, to protect the stills and condensers from nitrogenous fumes in the same way.

Procedure:

Clear 800 ml. Kjeldahl flasks of ammonia by concentrating to one-half its volume at least 600 ml. of magnesium oxide suspension.

Discard the residual suspension in the flasks, and use the unrinsed flasks immediately for the digestion. Pipet 10 ml. of a magnesia water solution containing 10 gms. of sugar per 100 ml. into the flask. (In analyzing sugars which are low in total nitrogen, larger quantities of the sugar should be taken.) Add about 1 gm. of copper oxide powder from the tip of a spatula, 25 ml. of concentrated sulfuric acid and, very cautiously, 25 ml. of potassium hydroxide solution. Heat the mixture cautiously with a small flame until frothing ceases and then with a strong flame until the carbon is completely oxidized and the solution is of a clear green color. The digestion is generally complete in about 2 hours. After the mixture has cooled, dilute with 400 ml. of magnesia water and make alkaline with 50 ml. of the saturated sodium hydroxide solution. Add at the same time a teaspoonful of the finely powdered magnesium oxide. Connect the flask immediately with the still and collect 200 ml. of distillate. This operation must be carried out in an ammonia-free atmosphere or in a trapped system. To each 100 ml. of distillate add 4 ml. of Nessler reagent as in ordinary water analysis, and after 15 minutes compare the colors which have developed with those which have been developed simultaneously from known quantities of the standard ammonium chloride solution diluted to 100 ml. with ammonia-free water.

An alternative method of measuring the ammonia obtained, which is not only convenient but economical if a large number of analyses are to be made, is to compare the color of the Nesslerized solutions in a spectrophotometer against distilled water. The transmittancy (T) at 510 mμ of each of a series of Nesslerized solutions containing known and differing quantities of ammonium chloride has been determined within 15 to 45

minutes after the addition of the reagent. If the transmittancy is expressed as a decimal and the logarithm of its reciprocal (log 1/T, or -log T) is plotted as ordinate against the quantity of nitrogen as ammonia in each solution as abscissa, a straight line is obtained which has a slope corresponding to an increase of 0.0530 in the -log T value for each increment of 0.01 mg. of nitrogen. The line as plotted does not pass through the origin, but a little above it, depending on the depth of color of the Nessler reagent itself. Hence, the position of the line on the graph must be determined with each new batch of Nessler reagent used. From the line so obtained, the quantity of nitrogen in an unknown is readily and easily determined by finding the -log T value of the Nesslerized distillate, without the necessity of making up new standard solutions for each set of determinations.

Calculate the results obtained by either method of measurement, after deducting the quantity of nitrogen as ammonia which is present in the reagents and which is determined by a blank determination on the reagents without sugar, to parts of nitrogen per million of sugar.

The nitrogen obtained by this method includes that present as nitrates. This was demonstrated by making determinations on a series of four solutions of nitrate-free sugar to which were added before the Kjeldahl digestions 0.0, 10, 20, and 40 micromilligrams of nitrogen as potassium nitrate. There were recovered 0.0, 10, 17, and 39 micromilligrams of nitrogen, respectively.

II. Protein Nitrogen

The protein nitrogen in juices has been extensively investigated by Vondrak and others. The amount of protein in white sugars is generally so small that it is impossible to obtain a definite color test

with protein reagents or to obtain more than a turbidity with such protein precipitants as copper sulfate, mercuric nitrate, phosphotungstic acid, or tannic acid. In two unusual sugars, sufficient protein was present to yield a biuret test when the precipitate obtained with copper sulfate was collected on a filter paper and moistened with a little dilute sodium hydroxide solution. When analyzed for protein nitrogen by the method to be described, the one giving the stronger biuret test was found to contain 8.6 p.p.m. of protein nitrogen.

Reagents:

Prepare the same reagents as were used for total nitrogen and also

Tannic Acid Solution: - Dissolve 10 gms. of tannic acid in distilled water and make up to 100 ml.

Procedure:

According to Vondrak, the tannic acid method of determining protein in the presence of sugar is the most accurate. To a solution of 25 gms. of the sugar in 100 ml. of water, add 5 ml. of the tannic acid solution. After heating the mixture on the steam bath for 2 hours to facilitate coagulation of the precipitate, filter on a quantitative filter paper. Wash the paper and the precipitate free from sugar with ammonia-free water, place in an 800 ml. Kjeldahl flask, and analyze for nitrogen by the method described above for total nitrogen. Determine blanks on a similar solution of protein-free sugar. Deduct the quantity of nitrogen found in the blanks from that found in the tannic acid precipitate, and calculate the result to parts of nitrogen per million.

III. Ammonia and Nitrates

The determination of ammonia in low-purity products has been thoroughly worked out by Baerts and Delvaux and by Vondrak, who have shown that the true value for ammonia may be obtained by distilling with magnesium oxide at 40° to 50° C. under reduced pressure. If the distillation is carried out at atmospheric pressure, the amides present are hydrolyzed to ammonia even by magnesium oxide. In white sugars, the ammonia present is so small that it is not deemed practical to use reduced pressure for the distillation. In fact, the values for ammonia are really the values of blanks for the nitrate determinations, representing the nitrogen from all compounds present which yield ammonia when treated with alkali under the conditions obtaining during the determination of nitrates. Of the various methods of determining nitrates, the only feasible one in which the large excess of sucrose does not interfere is that in which the nitrates are reduced to ammonia.

Reagents:

Magnesia Water: - Prepare as described under "Total Nitrogen."

Sodium Hydroxide Solution: - Prepare with magnesia water a solution containing 400 gms. of stick sodium hydroxide per liter.

Devarda's Alloy: - Grind the best grade of alloy fine enough to pass through a 50-mesh screen.

Nessler's Reagent.

Standard Ammonium Chloride Solution: - Prepare the standard solution as described under "Total Nitrogen."

Procedure:

Dissolve 2.5 gms. of sugar in 250 ml. of magnesia water in an 800 ml. Kjeldahl flask. Add 1 gm. of powdered Devarda's alloy, 50 ml. of

the sodium hydroxide solution, and a teaspoonful of the finely powdered magnesium oxide, and immediately connect the flask to the distillation apparatus. At the same time prepare a similar solution without the alloy and connect it to the still. After allowing them to stand at ordinary temperature for at least 30 minutes, when the vigorous evolution of hydrogen will have subsided, heat the mixtures slowly to boiling and distill as in the determination of total nitrogen until 200 ml. of distillate have been collected in Nessler tubes. Determine the ammonia in the distillate colorimetrically and correct for ammonia and nitrates in the reagents as found in blank determinations carried out without sugar. The amount of nitrogen as ammonia in the distillate from the mixture to which no alloy was added represents the nitrogen as "ammonia" in the sugar. When this quantity is deducted from that found in the distillate from the mixture to which the alloy was added, the difference is the nitrogen as nitrate in the sugar. Although Devarda's alloy reduces nitrites as well as nitrates, and therefore the nitrate value so found is really the sum of the nitrate and the nitrite nitrogens, no further correction is generally necessary, since the nitrite nitrogen is such a small quantity.

When Nessler's reagent is added to these distillates, a greenish color is generally formed, dur to volatile organic substances formed by the action of the alkali on the sugar. This coloration does not interfere with the development of the color due to ammonia, but its presence in the solutions precludes the measurement of the colors spectrophotometrically. If, however, both the standard ammonium chloride tube and the unknown tube are viewed through a Wratten K-3 No. 9 yellow light filter, the interference is overcome for colorimetric comparison and perfect matching is possible.

IV. Nitrites

Nitrites in sugar may be determined directly by the colorimetric method of Peter Griess with sulfanilic acid and alpha-naphthylamine, provided the standard solutions with which the colors are compared are made up with the same amount of nitrite-free sugar as is used in the unknowns. Use 20 gms. of sugar in 100 ml. of distilled water for the determination.

Since the amount of nitrite is so small (maximum found = 0.2 parts N per million; average of 30 typical sugars = 0.018 parts N per million), this determination has been abandoned as being unnecessary except in very special cases.

V. Amino Acids and Related Compounds

Ambler, Inter. Sugar J., 29, 382, 437, 498 (1927).
Ambler and Snider, Ind. Eng. Chem. (Anal. Ed.), 4, 37 (1932).

Amino acids in white sugars may be determined with ninhydrin, if there are present in the sugar no more than traces of reducing sugars. The amounts found have been so small that this determination has been abandoned except in special cases.

BARLEY CANDY TEST

Ambler, Manufacturing Confectioner, Jan. 1927, p. 17.
Ambler and Byall, Ind. Eng. Chem. (Anal. Ed.), 7, 168 (1935).

All barley candies made in the Carbohydrate Research Division are prepared according to the technic of Frederick W. Murphy described in The Candy Manufacturer for September 1921. It is a test that the candy maker himself can make in half an hour and from which he can derive his own conclusions without recourse to a chemist. The test approximates the actual conditions used in making hard candy, and is

one of the simplest and most reliable tests of the quality of a sugar intended for such use. It is flexible as regards conditions and technic. Hence, it is not necessary to follow the directions explicitly, so long as the test is always carried out in the same manner, with the same quantities of materials, and under the same conditions of heating, stirring, and so forth, down to the smallest detail. By developing a technic and adhering to it the results will be comparable, so that two testers, each using his own technic and scale for comparison, will rate the sugar the same, although the depth of color obtained by one with a particular sugar may not match that obtained by the other.

Apparatus for Candy Test:

Obtain, or have made, a copper casserole of the following specifications and dimensions: The bowl of the casserole is beaten out of 1/16 inch stock. It is 4-9/16 inches in diameter at the top, 2-1/4 inches in diameter at the bottom, and 2-9/16 inches deep. The sides are fairly straight, slightly rounded toward the bottom. Riveted on one side is a handle made of a copper tube, slightly tapering toward the bowl, 7/8 inch in diameter at the larger, outer end, and about 2 inches long. To prevent burning the hands, an oak or ash handle is fitted into the copper sheath of such a length that the whole handle is about 7 inches long.

Heat is obtained from a Chaddock burner. A gas pressure regulator is needed to insure a constant pressure of gas at the burner. A glass rod 1/4 inch in diameter, a watch glass 6 inches in diameter, a chemical thermometer which has been tested for accuracy at 175° C., and a 100 ml. graduated cylinder will also be needed.

For pouring and cooling the specimen, a polished copper slab, 14 inches by 14 inches, and 1/4 inch thick, is used. No grease will be needed on this as the candy may readily be lifted and removed from it if the polished surface is clean and dry.

The Test:

Place exactly one-half pound (227 gms.) of sugar in the casserole and pour over it exactly 90 ml. of distilled water. Place the casserole on the burner, with the flame so adjusted that the time required to complete the test is between 21 and 25 minutes.

Stir the sugar and water constantly until the sugar has completely dissolved, and then remove the glass rod. If the flame is properly regulated, the solution will boil in 5 to 5-1/2 minutes from the time it was placed on the burner. As soon as the solution boils, place a 6-inch watch glass over the casserole to prevent the sugar from crystallizing as evaporation takes place. (With some sugars the solution foams badly when it first begins to boil. If this happens to the extent that there is danger of its frothing over the sides of the casserole, lift the casserole from the burner for a moment until the foam subsides and then cautiously replace over the flame. After the excessive foaming is over, the solution will boil without danger of further overflowing and may be safely covered.)

Exactly 15 minutes after the casserole was placed over the flame, remove the watch glass and stir the boiling solution constantly and thoroughly with the thermometer until the latter registers 175° C. When this temperature is reached, pour the sirup immediately on to the clean, dry copper slab and allow the resulting candy plaque to cool. Break the candy up and place it in air-tight jars to keep for analysis.

Analyze the candy for color and pH as already described in previous paragraphs. Determine the moisture content by the standard method of drying on sand, using a solution of known concentration of the candy. Determine the invert sugar by the Munson-Walker method and the sucrose by the double polarization method, using (1) invertase for the inverting agent and (2) hydrochloric acid according to the Clerget method.

METHODS FOR ANALYSIS OF MASSECUITES

NITROGEN

I. Ammonia

Baerts and Delvaux, Sucr. Belge, 50, 52 (1930).
Chibnall, Biochem. J., 16, 349 (1922).

Dissolve 10 gms. of massecuite in 400 ml. of distilled water. Add 20 ml. of 50% sodium hydroxide solution and distill off the ammonia under reduced pressure, at a temperature of not over 60° C., into 100 ml. of 0.01 N hydrochloric acid. Back titrate the excess acid with 0.01 N sodium hydroxide solution. Run a blank on the reagents and water. Calculate as "nitrogen present as NH_3."

II. Nitrates

Baerts and Delvaux, l. c.
Chibnall, l. c.
"Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," (1930 Ed.), Sec. II, 35, p. 23.

To an exact duplicate of the solution prepared as for ammonia, add 1 gm. of Devarda's alloy and allow reduction to proceed for at least one hour. Distill off the ammonia, and titrate as in the ammonia determination. Deduct the ammonia found in a blank determination on water and reagents. Subtract the nitrogen found "as ammonia" in (I), obtaining the "nitrogen present as NO_3."

III. Total Nitrogen

Unpublished modification of Kjeldahl Method.

In an Erlenmeyer flask fitted with a trap containing dilute sulfuric acid to prevent the escape of ammonia, dissolve 10 gms. of massecuite in a small quantity of distilled water. Add 1 gm. of Devarda's alloy and 2 ml. of 50% sodium hydroxide solution and allow reduction to

proceed overnight. Unite the solutions in the trap and in the flask, acidify with 10 ml. of 1:1 sulfuric acid, boil off the excess of water, and analyze for nitrogen by Kjeldahl method, using 45 ml. of concentrated sulfuric acid and 6 to 8 gms. of potassium sulfate crystals. (Sufficient copper is present in the Devarda alloy to catalyze the oxidation without adding copper sulfate crystals.) Make the same determination on a blank of water and reagents. Calculate as percent of nitrogen.

IV. Protein Nitrogen

Unpublished

Dissolve 10 gms. of massecuite in about 20 ml. of distilled water. Add an equal volume of 5% trichloracetic acid, mix and allow to stand overnight. Filter, wash thoroughly and boil the combined filtrate and washings for about 15 minutes. Then neutralize the acid with sodium hydroxide solution, add an excess of 2 ml. of 50% sodium hydroxide solution and 1 gm. of Devarda's alloy, and proceed as for "Total Nitrogen." Determine nitrogen in the water and reagents in a blank determination. The difference of the value found for "Total Nitrogen" and that obtained from the filtrate after the trichloracetic acid treatment is the "Protein Nitrogen." Calculate as percent nitrogen.

SULFATES AND SULFITES

Unpublished; cf. Saillard, Rose Suppl. Circ. Hebd. #2240 (2-28-32); #2244 (3-27-32).

Weigh out a 50 gm. sample of massecuite and make up to 500 ml. with distilled water. To a 100 ml. aliquot add 10 ml. of 0.1 N iodine solution slowly with stirring. Allow to stand 5 minutes and add 10 ml. of 0.1 N sodium hydroxide solution, mix and allow to stand another 5 minutes. Acidify with 6 ml. of concentrated hydrochloric acid and filter. (There

must be a liberation of iodine upon acidification. If there is not, start the determination again, using a larger volume of the iodine solution.) Determine sulfates in the combined filtrate and washings with barium chloride as usual. Record as weight of barium sulfate.

To a second 100 ml. aliquot add 20 ml. of water and 5 ml. of concentrated hydrochloric acid and filter. Determine sulfates in the united filtrate and washings with barium chloride as usual. Record as weight of barium sulfate and, since this represents the sulfates originally present, calculate to percent of SO_3.

From the weight of barium sulfate obtained in the first determination subtract that obtained in the second, and calculate the difference to percent of SO_2.

ASH

"Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," (1935 Ed.), Sect. XXXIV, 9, p. 465.

Determine the lixiviated ash of the massecuite as usual, using a 10 gm. sample. Save the ash for the determinations of silica, calcium oxide and phosphates.

SILICA

"Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," (1935 Ed.), Sect. XII, 5, pp. 121-2.

Determine the silica in the lixiviated ash by dehydration with hydrochloric acid according to the usual analytical procedure. Combine the filtrate and washings, make to convenient volume, and aliquot for determinations of lime and of phosphates.

CALCIUM OXIDE

"Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," (1935 Ed.), Sect. XXVI, 18, p. 323.

Determine calcium oxide in an aliquot from the silica-free filtrate and washings, by precipitation of calcium oxalate and titration with permanganate as described in the determination of calcium oxide in sugars.

PHOSPHATES

Pemberton's Method, Sutton's "Volumetric Analysis," 11th Ed. (1924), pp. 313-5.

"Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," (1935 Ed.), Sect. II, 7-17, pp. 19-23.

Reagents:

Molybdate Solution: - Dissolve 100 gms. of molybdic acid in a mixture of 144 ml. of concentrated ammonium hydroxide and 271 ml. of water. Pour the solution slowly, with constant stirring, into a mixture of 489 ml. of concentrated nitric acid and 1148 ml. of water. Keep the final mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow ammonium phosphomolybdate. Decant from any sediment and preserve in a glass-stoppered bottle.

Standard Alkali: - 0.1 N NaOH.

Standard Acid: - 0.1 N HCl.

Procedure:

Make a second aliquot from the silica-free filtrate and washings alkaline with concentrated NH_4OH and acidify with concentrated HNO_3. Bring to a temperature of 50 to 60° C. and add the molybdate solution with stirring in sufficient quantity to completely precipitate the phosphates present. Let stand overnight. Filter and wash the precipi-

tate and paper free from acid. Place paper and precipitate in the beaker in which the precipitation was made, dissolve the yellow precipitate in a measured excess of the standard alkali, and titrate back with the standard acid, using phenolphthalein as indicator.

1 ml. of 0.1 N NaOH = 0.0003177 gm. P_2O_5. Calculate to percent of P_2O_5.

CHLORIDES

Ambler and Byall, Ind. Eng. Chem. (Anal. Ed.), 4, p. 379 (1932).
Browne and Gamble, Facts About Sugar, 17, p. 552 (1923).

Determine chlorides in a whole lixiviated ash from 10 gms. of massecuite by titration with standard silver nitrate in neutral solution using potassium chromate as indicator.

SODIUM AND POTASSIUM OXIDES

Determine these oxides by the same method as given in the methods for sugar. Calculate to percent Na_2O and percent K_2O.

METHODS FOR ANALYSIS OF BEET JUICES

The methods of analysis used for beet juices (pressed or diffusion) are generally the same as for massecuites, using a sample 2 or 3 times as great unless otherwise noted in the descriptions of the methods already given for massecuites, and except for the determination of sulfates. Since normally these juices contain no sulfites, the sulfates are determined in a third aliquot from the silica-free filtrate and washings of the lixiviated ash by precipitation as usual with barium sulfate.

Magnesium oxide, which is present only in traces in the sugars, and hence can be ignored, is present in the unlimed juices and is determined in the lixiviated ash as $Mg_2P_2O_7$ by the usual methods of quantitative analysis, after removal of the silica, iron and calcium.